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Atom removing from the Si(001)(2×1)-H surface under STM tip. Quantum-chemical approach

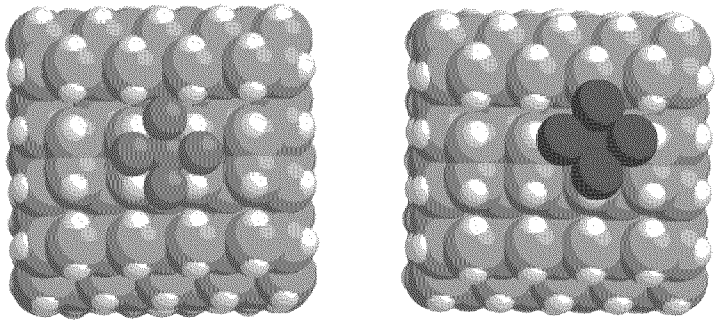
E. F. Sheka, E. A. Nikitina and M. Aono†
Russian Peoples' Friendship University, 117923 Moscow, Russia
† Institute of Chemical and Physical Research (RIKEN), Wako-shi, Japan
Department of Precision Science and Technology, Osaka University, Osaka, Japan

Abstract. Appropriate models are suggested for the supercluster simulating the Si(001)(2×1)-H surface as well as for the configuration of the electric field of an STM tip. A series of calculations have been performed for the supercluster in the electric field at different values of the field potentials and at different polarities. The electric field-stimulated desorption of hydrogen and silicon atoms has been observed at both polarities of the tip. The desorption reaction is a threshold one with the threshold potential somewhat higher at positively biased tip. The field impact is in a drastic redistribution of atomic charges in the substrate area under the tip that causes a weakening of interatomic bonding providing atom removing.

The equilibrated spin-singlet structure of the 306-atom supercluster, simulating partially hydrogenated Si(001) surface, is shown in Fig. 1. Initially spaced at 3.82 Å, silicon atoms of two central rows come together forming symmetrical dimers in the course of the total-energy minimum seeking [1]. The electric field was configured by a set of point charges in a model of a sharp one-and-four tungstem atom tip whose position is shown in Fig. 1. The tip was placed 5 Å above the topmost silicon atoms. Its position in the horizontal place varied.

Electrostatic potential $\varphi(x, y, z)$ stimulated by the tip within a substrate is determined as [2]

$$\varphi(x, y, z) = \sum_i q_i / 4\pi\varepsilon\varepsilon_0 [(x - x_i)^2 + (y - y_i)^2 + (z - z_i)^2]^{1/2}$$



(a) (b)

Fig. 1. Top view on the equilibrated supercluster simulating the Si(001)(2x1)-H surface. Tip in position (a) and (b) is placed 5 Å above the top silicon atoms.

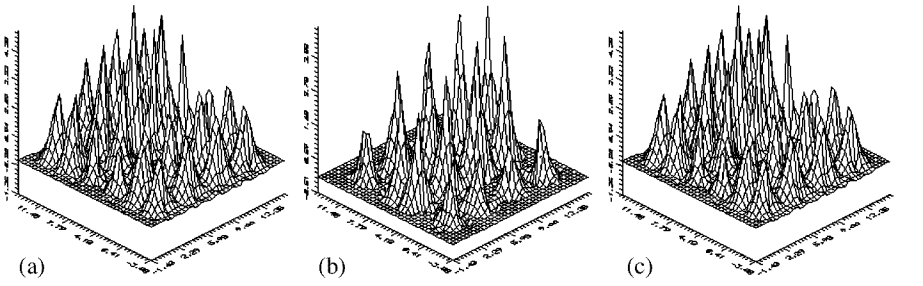


Fig. 2. Tip-stimulated potential distribution over the topmost hydrogen (a), (c) and silicon (b) atoms of the substrate. (a) and (b). Tip consists of five point charges of +0.5 a.u. each. Potential maximum constitutes +7.7 eV. (c). Conical tip is biased by +10 V. Potential maximum is +5.92 eV. Tip is in position (b) of Fig. 1.

where q_i is a point charge positioned at (x_i, y_i, z_i). The components of the electric field vector $\mathbf{E} = -\nabla\varphi$ are determined as

$$E_x = \sum_i q_i(x - x_i)/4\pi\varepsilon\varepsilon_0[(x - x_i)^2 + (y - y_i)^2 + (z - z_i)^2]^{3/2}$$

$$E_y = \sum_i q_i(y - y_i)/4\pi\varepsilon\varepsilon_0[(x - x_i)^2 + (y - y_i)^2 + (z - z_i)^2]^{3/2}$$

$$E_z = \sum_i q_i(z - z_i)/4\pi\varepsilon\varepsilon_0[(x - x_i)^2 + (y - y_i)^2 + (z - z_i)^2]^{3/2}$$

The field on the supercluster atoms had a hill-like configuration with the hill high as bigger as nearer the atoms are to the top layer. As for the atoms positioned in the same layer, the field is non-uniform and depends on a relative position of the tip with respect to the atom considered. The field strength was controlled by the point charge values. Fig. 2 shows the field distribution over the topmost hydrogen and silicon atoms for the tip charged positively. Analogous picture is observed for the negatively charged tip.

Experimentally, one operates with a biased not charged tip. Electrostatic potential $\varphi(x, y, z)$ in a substrate stimulated by a biased tip is determined by the Poisson equation [3]

$$\varepsilon\varepsilon_0\Delta\varphi = e(n - p - N)$$

(n, p, and N are related concentrations of electrons, holes, and impurities) under conditions when the potential at a conical tip $\varphi = V$ is constant while the potential in the space between the substrate and the tip is obeyed to the Laplace equation $\Delta\varphi = 0$.

A series of total-energy minimisation considered in the framework of a quantum-chemical software DUQUFIELD [4, 5] based on a semi-empirical method AM1 has been performed for varied strengths of the field at both polarities of the tip. A removing of one (sometimes two) hydrogen atom is observed at both polarities with somewhat different absolute values of the threshold field (about −6.84 V and +7.70 V). The threshold value depends on the relative position of the tip and the atom considered rather slightly, while being always 10–15% bigger by absolute value for the positively biased tip.

The field impact is in a drastic redistribution of atomic charges in the substrate area under the tip that becomes more pronounced when the potential increases. This causes a

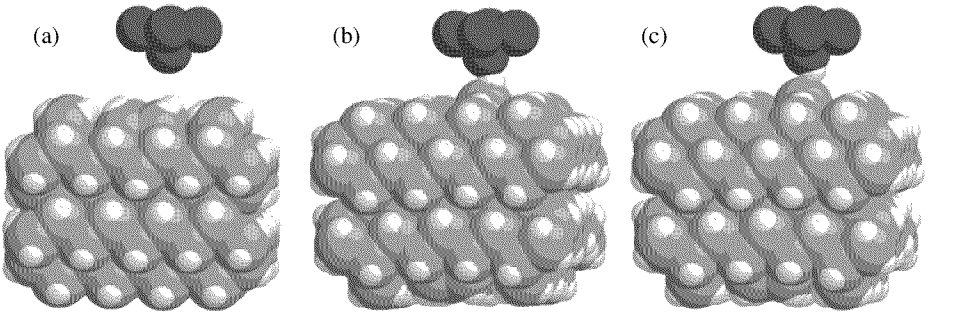


Fig. 3. Successive steps of a hydrogen atom removing at a threshold (negatively biased tip). Starting (a), intermediate (b), and final (c) step, respectively.

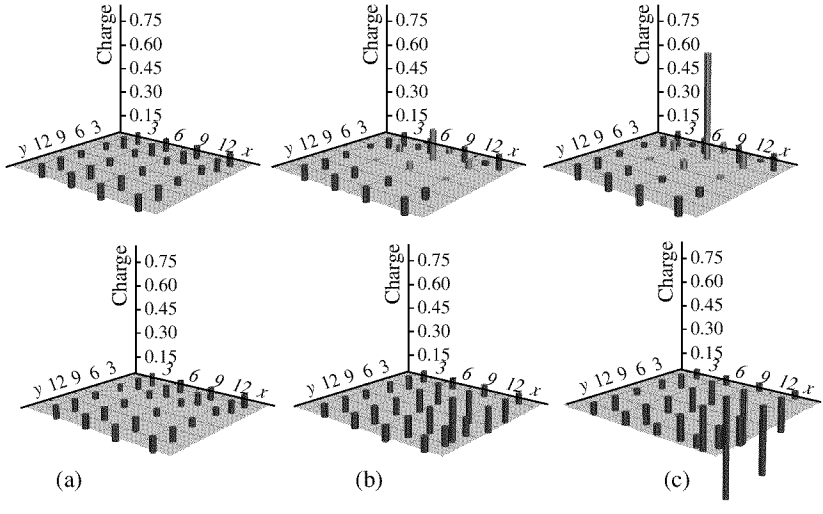
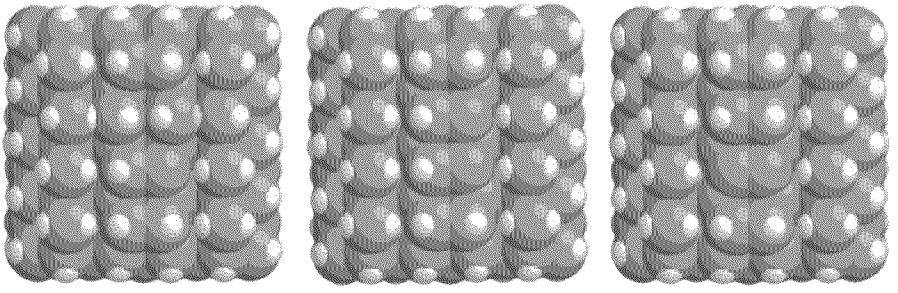


Fig. 4. Distribution of atom charge over the topmost hydrogen atoms under the negatively (top) and positively (bottom) biased tip in position (b) of Fig. 1. Zero (a), intermediate (b), and threshold (c) field.

weakening of interatomic bonding providing atom removing. Fig. 4 shows the effect for the topmost hydrogen atoms under the negatively and positively biased tip. As seen from the figure, the redistribution concerns the same atoms in both cases being, however, opposite by sign.

If the field continues to act after an H atom is going away, a removing of a silicon atom proceeds. Similarly to the hydrogen atoms, the field-stimulated desorption of silicon atoms is caused by a drastic redistribution of the relevant atomic charge when approaching the threshold field.

If the field is switched off after the hydrogen atom removing, a relaxation of the surface structure takes place completed by the formation of energetically stable local defects. Typical defects obtained are shown in Fig. 5. Symmetric dimers are formed in all cases with the difference that the Si–Si spacing in first two cases constitutes 2.42 and 2.38 Å while it is of 2.16 Å in the last case. The former values are typical for a single Si–Si bond while the latter is characteristic for a double Si=Si bond [1] that is formed at the surface.



(a) (b) (c)

Fig. 5. Equilibrated defect structures formed after one (a) and two (b,c) hydrogen atom removing. Negatively (a, b) and positively (c) biased tip in position (a) of Fig. 1.

The obtained results on the field-stimulated desorption of hydrogen atoms from the Si(001)(2×1)-H surface are well consistent with recent experimental findings [6–8]. Therefore, the suggested static-field desorption mechanism is a well-supported alternative to the previously discussed dynamic one. The latter relates the atom desorption to vibrational heating of the atom by inelastic scattering of either tunnelling electrons [9] or tunnelling holes [8] with the corresponding resonances on the substrate in the case of negatively and positively biased tip, respectively.

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